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13. ABSTRACT (Maximum 200 words) New, unusual perfluorinated organic molecules have been synthesized and their chemistry has been examined. Reaction mechanisms of fluorocarbon derivatives have been investigated, and new synthetic methodology has been developed. The nature and chemistry of excited states as well as ground states have been explored. 93-16835 					
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**Final Report
for
Air Force Office of Scientific Research Grant AFOSR-90-0015**

Grant Title: Synthesis and Chemistry of Novel Cyclic
Fluorocarbons

Period Covered: November 1, 1989 to October 31, 1992

Institution: Dartmouth College, Hanover, N. H. 03755

Principal Investigator: David M. Lemal

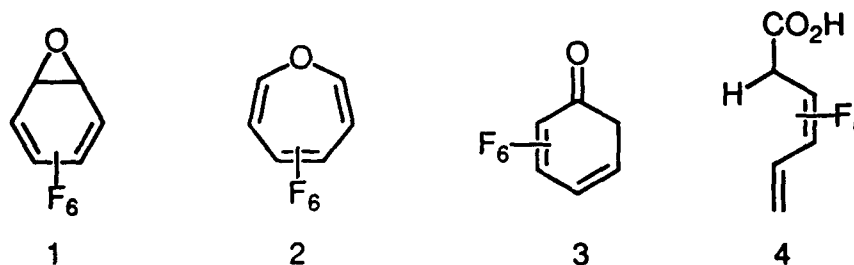
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Summary of Accomplishments

The overarching objective of the research carried out under AFOSR-90-0015 was to gain greater knowledge and understanding of the consequences of perfluorination on the nature and reactivity of organic compounds. This quest was pursued with a multi-pronged approach. Our work has entailed the synthesis of new fluorocarbons and fluorocarbon derivatives, together with exploration of their chemistry; mechanistic studies of reactions of organofluorine compounds; development of new synthetic methodology; and an investigation in electronic spectroscopy. The sharp contrasts in chemistry which we have found between the perfluoro compounds and their hydrocarbon counterparts have served both to illuminate the special character of fluorine as substituent in organic molecules and to suggest synthetic routes to fluorocarbons which are not possible for hydrocarbons. The principal projects to which our efforts have been devoted are summarized below.

Hexafluorobenzene Oxide (1) and Hexafluorooxepin(2). Oxide 1 was synthesized in several steps from hexafluorobenzene. The fragility of this molecule explains earlier failures in our laboratory and in England to synthesize it. Upon gentle heating or simply standing in a polar solvent it rearranges to dienone 3, a transformation which also occurs upon triplet sensitization or direct photolysis with ultraviolet light. The product found under the last set of conditions was actually the acid 4, but this was shown to form when 3 is photolyzed. Pentafluorophenol is produced by reduction of oxide 1 under extremely mild conditions, e.g. sodium iodide in acetone at room temperature.

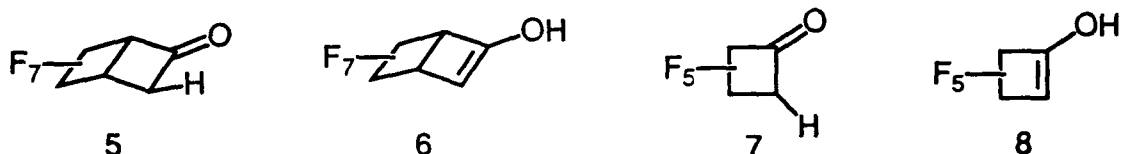


A dynamic ¹⁹F NMR study revealed that a very small amount of oxepin 2 exists in rapid equilibrium with 1 (~3% in chlorobenzene at 55°). In contrast, oxepin itself predominates in equilibrium with benzene oxide in nonpolar solvents. Since fluorine substitution strongly destabilizes cyclopropane rings, we had assumed that 1, with its 3-membered ring, would be greatly overshadowed by 2 at equilibrium. The discrepancy here between theory and experiment is intriguing, and it begs for further investigation of fluorinated oxiranes.

A Novel Keto-Enol System. We discovered that ketone 5, synthesized as an intermediate in an approach to bicyclo[2.1.0]pentane, existed in equilibrium with its enol tautomer 6. Remarkably,

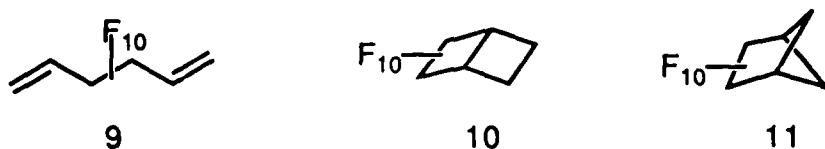
the enol was found to be stabler than the keto form in mildly Lewis basic solvents such as acetonitrile, tetrahydrofuran and ether. *This behavior is unique in organic chemistry, we believe, for a simple keto-enol system. These tautomers are also strikingly acidic, as they are stoichiometrically deprotonated by N-methylpyrrolidone, a neutral amide.*

The closest analog to this system in the literature is the pair of isomers **7** and **8**, prepared by Russian workers. Amazingly, the Russians were unable to interconvert these very stable isomers,



so their relative stability remains unknown. We therefore attempted to obtain **7** and **8** to resolve the stability question. Though we could not repeat the Russian synthesis of the enol, we modified the route and secured a sample for study. Like the Russians, we were unable to transform it into the ketone, perhaps because the enol is much stabler. Current efforts are devoted to acquiring the ketone, with the hope of effecting the reverse isomerization. The bizarre behavior of **5-8** sets the stage for interesting and revealing investigations of the relationship between structure on the one hand and, on the other, such properties as energy content and acidity of perfluorinated keto-enol systems.

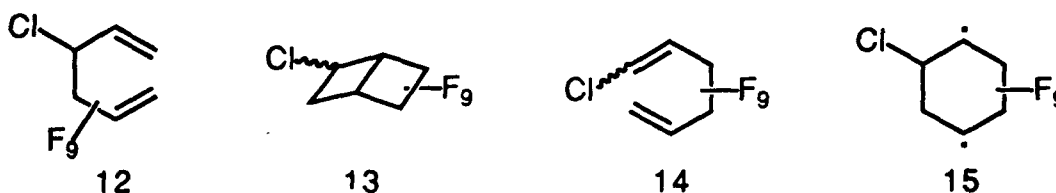
Thermal and Photochemistry of C₆F₁₀ Valence Isomers. Pyrolysis of perfluoro-1,5-hexadiene (**9**) at 250°C produced an equilibrium mixture of **9** and its bicyclic isomer **10** in which the latter predominated. At higher temperatures the diene isomerized quantitatively to **11**. In contrast, the hydrocarbon counterparts of **10** and **11** isomerize completely at high



temperatures to 1,5-hexadiene. Mercury photosensitization of diene **9** in the vapor phase yielded **11** as the dominant product accompanied by **10** in a rather clean reaction. Again this behavior contrasts markedly with that of the 1,5-hexadiene itself. Mercury sensitization of the hydrocarbon yields a welter of products even when carried out to low conversions. These observations suggest that *thermolysis and photolysis of perfluorodienes and polyenes may prove to be a fruitful source of presently unknown bi- and polycyclic fluorocarbons via cyclizations without parallel in*

hydrocarbon chemistry. Given present paucity of synthetic methods for assembling perfluorinated carbon skeletons, this would be a very welcome development.

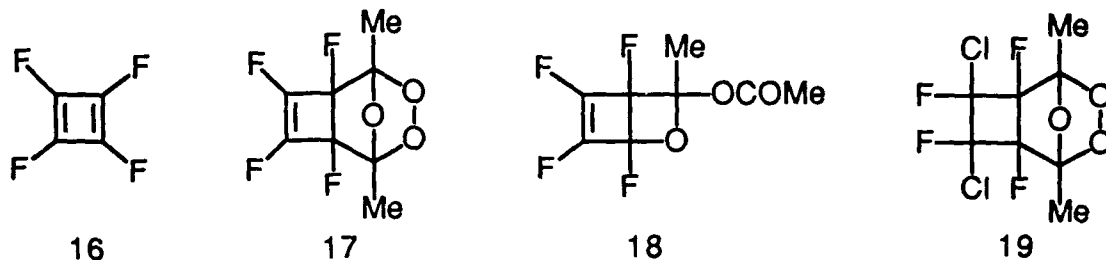
Mechanism of the Cope Rearrangement of Perfluorodienes. Extensive investigations have established to the satisfaction of most researchers that 1,5-hexadiene undergoes the Cope rearrangement via a concerted pathway. We were curious about the mechanism of the corresponding transformation of perfluoro-1,5-hexadiene. Since its Cope rearrangement would be degenerate and thus undetectable, we synthesized the labelled analog **12**. Interestingly, pyrolysis of **12** at temperatures over 200°C yielded principally the endo and exo isomers of **13** accompanied by only minor amounts of the Cope product **14** (E and Z forms). Heating **14** also gave **13**.



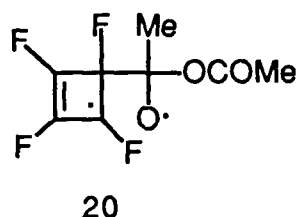
Bicyclization of the dienes undoubtedly proceeds via 1,4-biradical **15**, and it follows that the transition state for a hypothetical concerted Cope rearrangement pathway must lie at substantially higher energy than the transition states connecting the dienes with biradical **15**. *Thus, the Cope rearrangement of perfluorodienes proceeds stepwise, in contrast to that of the corresponding hydrocarbons.* This finding can be understood in terms of the driving force for highly fluorinated double bonds to become saturated, i.e. for sp^2 carbon to become sp^3 hybridized, for in the transition state leading to the 1,4-biradical the carbons involved in sigma bond breaking and making are either sp^3 hybridized or close to it. In a concerted transition state they would be expected to be roughly halfway between the two hybridizations.

A New, Mild and Selective Dehydrohalogenating Agent. In part through serendipity, we discovered that lead (II) oxide reacts with hydrated lithium bromide in acetonitrile to yield a white solid which we believe to be a hydrated lithium hydrogen bromoplumbite. This mildly basic reagent effects elimination of HCl and HBr from substrates with modestly acidic hydrogen, apparently via the E2 mechanism. While it can bring about elimination via a synperiplanar transition state, an antiperiplanar transition state is preferred, as expected. The bromoplumbite should be useful when a gentle and highly selective dehydrohalogenating agent is required.

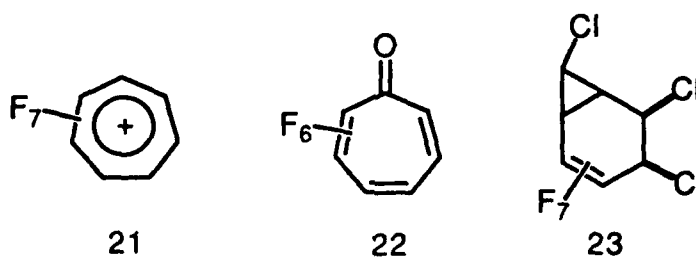
An Approach to Tetrafluorocyclobutadiene (16). Though we synthesized this theoretically interesting molecule many years ago, our routes to it were not well suited for a detailed investigation of the diene. We expected that ozonide **17** would be an excellent photochemical precursor for **16**, and we were finally able to obtain the ozonide after much difficulty. Unfortunately, photolysis of **17** yielded, not **16**, but a product we believe to be the oxetane acetate **18**. This is a really



surprising result, as ozonide photolysis has produced other cyclobutadienes. The closely related ozonide **19** underwent smooth photolysis to give the expected 3,4-dichlorocyclobutene, so the problem is specifically with the cyclobutadiene. Formation of oxetane **18** presumably occurs via cleavage of just one of the bonds to the fluorinated ring, giving biradical **20**, which then cyclizes instead of fragmenting to diene plus acetic anhydride. Failure of the fragmentation process may signify that the tetrafluoro compound is unusually unstable even for a cyclobutadiene.



Perfluorotropone. In the course of attempts to develop a more practical synthesis of the perfluorotropylium ion (**21**) than our original route, we found a new route to perfluorotropone (**22**). Addition of chlorofluorocarbene to *cis*-5,6-dichloroperfluoro-1,3-cyclohexadiene, which we have synthesized in >60% yield from hexafluorobenzene, gave trichloride **23**. Treatment of **23**

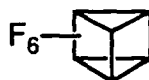


with copper bronze in dimethyl sulfoxide effected reductive ring opening to tropone **22**. The reaction probably occurred via the ion **21**, which was intercepted by DMSO to introduce the oxygen. Study of the tropone will be interesting in its own right, and this ketone may function as a precursor for ion **21** (via conversion to perfluorotropilidene with sulfur tetrafluoride).

Hexafluorobenzene Excited States and C₆F₆ Photochemistry. Hexafluorobenzene is transformed in high yield in the vapor phase by ultraviolet light into the dewarbenzene (24). In hopes of preparing the unknown and undoubtedly labile hexafluoroprismane (25), we attempted photocyclization of 24 at low temperatures. Disappointingly, both direct and sensitized photolysis of the dewarbenzene only led back to the benzene.



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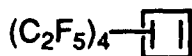


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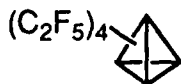
In examining the fluorescence of hexafluorobenzene in a nanosecond flash absorption/emission apparatus, we were struck by the short duration of the emission (~2 ns), its ~100 nm Stokes shift and its great spectral breadth. Together with other information from the literature, these (known) observations led us to the surmise that the emitting state -- and thus the lowest lying singlet state -- of hexafluorobenzene is not a π, π^* state but a π, σ^* state. *This assignment has important implications for the photochemistry of hexafluorobenzene and other highly fluorinated benzenes, and its contrast with that of benzene itself.* In particular, this assignment would explain the facile formation of dewarbenzenes and the absence of benzvalenes (which arise from the B_{2u} state, S₁ of benzene).

We attempted to confirm our assignment by examining the polarization of hexafluorobenzene's electronic absorption bands in the near ultraviolet using stretched polyethylene films impregnated with the benzene. Unfortunately, despite much effort we were unable to obtain high enough concentrations of oriented molecules by this method to determine the polarizations, but we hope to accomplish this with the help of Prof. J. Michl by using a more sophisticated method.

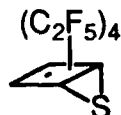
Perfluorotetraethylcyclobutadiene (26). This molecule is of interest as a cyclobutadiene symmetrically substituted with powerful electron-withdrawing groups, which should render it extraordinarily electrophilic even for a cyclobutadiene. The bulk of these groups may serve to inhibit dimerization sufficiently that 26 can be studied at ordinary temperatures, and may also promote photocyclization of the diene to perfluorotetraethyltetrahedrane (27). This would be the first tetrahedrane bearing electron-withdrawing groups, and its properties should contrast sharply with those of the few known tetrahedranes.



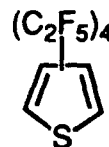
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We therefore embarked on an approach to cyclobutadiene **26**, a route which proceeded via dewarhiophene **28**. Synthesis of thiophene **29** was required, and this was to be accomplished by perfluoroalkylation of tetraiodothiophene. After initial problems with the copper-mediated coupling reaction, we obtained evidence for partial perfluoroalkylation and hope to achieve introduction of all four perfluoroethyl groups in the future.

Publications Based on AFOSR-Supported Work

Numbers 1-5 and 7 are the result of work carried out with AFOSR support antedating AFOSR-90-0015.

1. Soelch, R. R.; McNierney, E.; Tannenbaum, G. A.; Lemal, D. M. "Synthesis and Chemistry of Highly Fluorinated Bicyclo[2.2.0]hexenones", *J. Org. Chem.* **1989**, *54*, 5502-11.
2. Dailey, W. P.; Correa, R. A.; Harrison, E., III; Lemal, D. M. "The 5,6-Dichlorohexafluorocyclohexadienes: Hexafluorobenzene Synthons", *J. Org. Chem.* **1989**, *54*, 5511-6.
3. Dailey, W. P.; Ralli, P.; Wasserman, D.; Lemal, D. M. "1,2-Cycloadditions to cis-5,6-Dichlorohexafluorocyclohexa-1,3-dienes", *J. Org. Chem.* **1989**, *54*, 5516-22.
4. Roberts, B. E.; Goldman, G. D.; Lemal, D. M. "State-Dependent Photochemistry of Highly Fluorinated Bicyclo[4.2.0]octa-2,4-dienes", *J. Fluor. Chem.* **1990**, *48*, 353-60.
5. Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. "Valence Isomerization Equilibria of Highly Fluorinated Cycloocta-1,3,5-trienes", *J. Am. Chem. Soc.* **1990**, *112*, 5986-90.
6. Takenaka, N. E.; Hamlin, R.; Lemal, D. M. "Hexafluorobenzene Oxide and Hexafluorooxepin", *J. Am. Chem. Soc.* **1990**, *112*, 6715-6.
7. Lemal, D. M.; Klopotek, D. L.; Wilterdink, J. L.; Saunders, W. D. "Carbonyl Chemistry of Tetrafluorocyclopentadienone", *J. Org. Chem.* **1991**, *56*, 157-60.
8. Takenaka, N.E.; Lemal, D.M. "The Perfluorobenzene Oxide/Perfluorooxepin System" in *Synthetic Fluorine Chemistry*; Olah, G.; Chambers, R.D.; Prakash, G.K.S., Eds.; Wiley: New York, 1992.
9. Jing, N.; Lemal, D.M. "The Mechanism of the Cope Rearrangement of Perfluorodienes", *J. Am. Chem. Soc.*, accepted for publication.
10. Correa, R.A.; Jing, N.; Lemal, D.M. "Interrelationships Among C₆F₁₀ Valence Isomers", *J. Org. Chem.*, accepted for publication.

Manuscripts in Preparation

Number 2 is the result of work carried out with AFOSR support antedating AFOSR-90-0015.

1. Takenaka, N.E.; Hamlin, R.E.; Lemal, D.M. "1,8H-Perfluorocyclooctatetraene and its Congeners. Dynamic Equilibrium Among Four Valence Isomers" (*J. Org. Chem.*)

2. Goldman, G.D.; Roberts, B.E.; Cohen, T.D.; Barefoot, A.C., III; Lemal, D.M. "1,2- and 1,8-Dichlorohexafluorocyclooctatetraene: Stable Bond-Shift Isomers" (*J. Org. Chem.*)
3. Kendall, J.T.; Lemal, D.M. "A New Mild and Selective Dehydrohalogenating Agent" (*Tetrahedron Lett.*)
4. Correa, R.A.; Lemal, D.M. "A Novel Perfluorinated Keto-Enol System" (*Tetrahedron Lett.*)

Coworkers

Postdoctoral Associate

Jing, N.

Graduate Students

Correa, R. A.

Ganser, S.

Kendall, J.

Takenaka, N.

Zhang, Y.

Ph.D. Theses and Degrees Awarded

Takenaka, N.E., Part I. "Approaches to the Synthesis of Perfluorosemibullvalene" Part II. "Synthesis and Studies of Perfluorobenzene Oxide / Perfluorooxepin", 199

Correa, R.A., "Synthesis of Highly Fluorinated Bicyclo[2.2.0]hex-2-ene Derivatives", 1990.

Kendall, J. T., Part I. "Synthetic Approaches to the Perfluorotropylium Ion" Part II. "A New, Mild and Selective Dehydrohalogenating Reagent", 1991.

Invited Lectures on AFOSR-Grant-Related Work

At Colleges and Universities

Boston College	April, 1990
University of Massachusetts	October, 1990
Rensselaer Polytechnic Institute	December, 1990
Wesleyan University	December, 1991

At Meetings

17th Annual Ontario-Quebec Physical Organic Minisymposium, Quebec City, November, 1989

International Chemical Congress of Pacific Basin Societies, Honolulu, December, 1989

Symposium on Synthetic Fluorine Chemistry sponsored by the Loker Hydrocarbon Institute, Los Angeles, February, 1990

Tenth Winter Fluorine Conference, St. Petersburg, February, 1991
Eleventh Winter Fluorine Conference, St. Petersburg, January, 1993

Presentations by Coworkers

Correa, R.A., oral presentation at 199th National Meeting of the American Chemical Society, Boston, April, 1990

Jing, N., poster presentation at the Eleventh Winter Fluorine Conference, January, 1993

Zhang, Y., poster presentation at the Eleventh Winter Fluorine Conference, January, 1993

David M. Lemal